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(54) Title: DESULFURIZATION AND NOVEL SORBENTS FOR SAME

(57) Abstract: A sorbent composition is provided which can be used for the desulfurization of a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel. The sorbent composition contains a support component, an attrition-resistance-enhancing component, and a promoter component. The promoter component is present in a reduced valence state. Such sorbent composition can be generally prepared by a process of incorporating a support component and an attrition-resistance-enhancing component with a promoter component followed by reducing to thereby reduce the valence state of the promoter component.

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DESULFURIZATION AND NOVEL SORBENTS FOR SAME
BACKGROUND OF THE INVENTION

This invention relates to a sorbent composition, a process of making a sorbent composition, and to a process of using a sorbent composition for the removal of sulfur
5 from a hydrocarbon-containing fluid.

The need for cleaner burning fuels has resulted in a continuing world-wide effort to reduce sulfur levels in hydrocarbon-containing fluids such as gasoline and diesel fuels. The reduction of sulfur in such hydrocarbon-containing fluids is considered to be a means for improving air quality because of the negative impact the sulfur has on the performance
10 of sulfur-sensitive items such as automotive catalytic converters. The presence of oxides of sulfur in automotive engine exhaust inhibits and may irreversibly poison noble metal catalysts in the converter. Emissions from an inefficient or poisoned converter contain levels of non-combusted, non-methane hydrocarbons, oxides of nitrogen, and carbon monoxide. Such emissions are catalyzed by sunlight to form ground level ozone, more
15 commonly referred to as smog.

Most of the sulfur in a hydrocarbon-containing fluid such as gasoline comes from thermally processed gasolines. Thermally processed gasolines such as, for example, thermally cracked gasoline, visbreaker gasoline, coker gasoline and catalytically cracked gasoline (hereinafter collectively referred to as "cracked-gasoline") contains, in part,
20 olefins, aromatics, sulfur, and sulfur-containing compounds.

Since most gasolines, such as for example automobile gasolines, racing gasolines, aviation gasolines, boat gasolines, and the like contain a blend of, at least in part, cracked-gasoline, reduction of sulfur in cracked-gasoline will inherently serve to reduce the sulfur levels in most gasolines such as, for example, automobile gasolines, racing
25 gasolines, aviation gasolines, boat gasolines, and the like.

The public discussion about gasoline sulfur has not centered on whether or not sulfur levels should be reduced. A consensus has emerged that lower sulfur gasoline reduces automotive emissions and improves air quality. Thus, the real debate has focused on the required level of reduction, the geographical areas in need of lower sulfur gasoline,
30 and the time frame for implementation.

As the concern over the impact of automotive air pollution continues, it is clear

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that further efforts to reduce the sulfur levels in hydrocarbon-containing fluids such as gasolines, more particularly automotive gasolines, will be required. While the current gasoline products contain about 330 parts per million (ppm) sulfur by weight, the U. S. Environmental Protection Agency recently issued regulations requiring the average sulfur
5 content in gasoline to be less than 30 ppm average with an 80 ppm maximum. By 2006, the standards will effectively require every blend of gasoline sold in the United States to meet the 30 ppm level.

In addition to the need to be able to produce low sulfur content automotive fuels, there is also a need for a process which will have a minimal effect on the olefin content of
10 such fuels so as to maintain the octane number (both research and motor octane number). Such a process would be desirable since saturation of olefins greatly affects the octane number. Such adverse effect on olefin content is generally due to the severe condition normally employed, such as during hydrodesulfurization, to remove thiophenic compounds (such as, for example, thiophenes, benzothiophenes, alkyl thiophenes, alkyl
15 benzothiophenes, alkyl dibenzothiophenes and the like) which are some of the most difficult sulfur-containing compounds to be removed from cracked-gasoline. In addition, there is a need to avoid a system wherein the conditions are such that the aromatic content of the cracked-gasoline is also lost through saturation. Thus, there is a need for a process wherein desulfurization is achieved and the octane number is maintained.

20 In addition to the need for removal of sulfur from hydrocarbon-containing fluids such as cracked-gasoline, there is also presented to the petroleum industry a need to reduce the sulfur content in other hydrocarbon-containing fluids such as diesel fuel. In removing sulfur from diesel fuel by hydrodesulfurization, the cetane is improved but there is a large cost in hydrogen consumption. Such hydrogen is consumed by both hydro-
25 desulfurization and aromatic hydrogenation reactions.

Thus, there is a need for a process of desulfurization without a significant consumption of hydrogen so as to provide a more economical process for the treatment of hydrocarbon-containing fluids such as cracked gasoline and diesel fuel.

As a result of the lack of success in providing a successful and economically
30 feasible process for the reduction of sulfur levels in hydrocarbon-containing fluids such as cracked-gasoline and diesel fuel, it is apparent that there is still a need for a better process

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for the desulfurization of such hydrocarbon-containing fluids which has minimal effect on octane levels while achieving high levels of sulfur removal.

Traditionally, sorbent compositions used in processes for the removal of sulfur from hydrocarbon-containing fluids have been agglomerates utilized in fixed bed applications. Because of the various process advantages of fluidized beds, hydrocarbon-containing fluids are sometimes used in fluidized bed reactors. Fluidized bed reactors have advantages over fixed bed reactors such as better heat transfer and better pressure drop. Fluidized bed reactors generally use reactants that are particulates. The size of these particulates is generally in the range of about 1 micrometer to about 1000 micrometers. However, the reactants used generally do not have sufficient attrition resistance for all applications. Consequently, finding a sorbent with sufficient attrition resistance that removes sulfur from these hydrocarbon-containing fluids and that can be used in fluidized, transport, moving, or fixed bed reactors is desirable and would be of significant contribution to the art and to the economy.

SUMMARY OF THE INVENTION

It is desirable to provide a sorbent composition that can be used for the removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel.

Again it is desirable to provide a sorbent composition comprising a promoter component selected from the group consisting of metals, metal oxides, and the like and combinations thereof.

Yet again it is desirable to provide a method of making a novel sorbent composition which is useful in the desulfurization of a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel.

Once again it is desirable to provide a novel sorbent composition having an enhanced attrition resistance when utilized in the desulfurization of a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel.

Again it is desirable to employ such novel sorbent composition and a process for the removal of sulfur, such as that found in sulfur-containing compounds, from a hydrocarbon-containing fluid, such as cracked-gasoline or diesel fuel, which minimizes the consumption of hydrogen and minimizes the saturation of olefins and aromatics contained in such hydrocarbon-containing fluid.

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Yet again it is desirable to provide a desulfurized cracked-gasoline that contains less than about 100 parts per million of sulfur based on the weight of the desulfurized cracked-gasoline and which contains essentially the same amount of olefins and aromatics as are in the cracked-gasoline from which such desulfurized cracked-gasoline was made.

5 Again it is desirable to provide a desulfurized diesel fuel wherein the cetane is improved and such desulfurized diesel fuel contains essentially the same amount of olefins and aromatics as are in the diesel fuel from which such desulfurized diesel fuel was made.

10 The present invention is based upon our discovery that through the utilization of an attrition-resistance-enhancing component present in an attrition-resistance-enhancing amount in a sorbent composition, there is achieved a novel sorbent composition which permits the ready removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel with a minimal effect on the octane rating of the treated hydrocarbon-containing fluid and where such sorbent composition has an enhanced
15 attrition resistance compared to a sorbent composition that does not contain such attrition-resistance-enhancing component.

20 In one aspect of the present invention there is provided a novel sorbent composition suitable for the desulfurization of a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel. Such novel sorbent composition comprises a support component, a promoter component selected from the group consisting of metals, metal
25 oxides, and the like and combinations thereof wherein the valence of such promoter component is substantially reduced and such reduced-valence promoter component is present in an amount which is effective in the removal of sulfur from a hydrocarbon-containing fluid, and an attrition-resistance-enhancing component present in an amount which is effective in enhancing the attrition resistance of a sorbent composition of the
30 present invention.

30 In accordance with another aspect of the present invention, there is provided a process for the preparation of a novel sorbent composition which comprises: contacting a support component, preferably such support component comprises zinc oxide, silica, and alumina, and an attrition-resistance-enhancing component to form a mixture selected
30 from the group consisting of a wet mix, a dough, a paste, a slurry, and the like;

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particulating such mixture so as to form a particulate selected from the group consisting of a granulate, an extrudate, a tablet, a sphere, a pellet, a microsphere, and the like; drying such particulate to form a dried particulate; calcining such dried particulate to form a calcined particulate; incorporating a promoter component selected from the group
5 consisting of metals, metal oxides, and the like and combinations thereof on, in, or with such dried and calcined particulate to form a promoted particulate; drying such promoted particulate to form a dried promoted particulate; calcining such dried promoted particulate to form a calcined promoted particulate; and reducing such calcined promoted particulate with a suitable reducing agent, such as hydrogen, so as to produce a sorbent composition
10 having a substantially zero-valence promoter component incorporated on, in, or with such sorbent composition in an amount which is effective in removing sulfur from a hydrocarbon-containing fluid. The attrition resistance of the sorbent composition is enhanced by providing an effective concentration of an attrition-resistance-enhancing component.

15 In accordance with a further aspect of the present invention, there is provided a process for the desulfurization of a hydrocarbon-containing fluid selected from the group consisting of cracked-gasoline, diesel fuel, and the like and combinations thereof which comprises desulfurizing in a desulfurization zone such hydrocarbon-containing fluid with a sorbent composition, separating the desulfurized hydrocarbon-containing fluid and the
20 sulfurized sorbent composition, regenerating at least a portion of the sulfurized sorbent composition to produce a regenerated, desulfurized sorbent composition; activating at least a portion of the regenerated, desulfurized sorbent composition to produce an activated, regenerated, desulfurized sorbent composition; and thereafter returning at least a portion of the activated, regenerated, desulfurized sorbent composition to the
25 desulfurization zone.

Other objectives and advantages of the present invention will be apparent from the detailed description of the invention and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

The term "gasoline" denotes a mixture of hydrocarbons boiling in the range of
30 from about 100°F to about 400°F, or any fraction thereof. Examples of suitable gasoline include, but are not limited to, hydrocarbon streams in refineries such as naphtha, straight-

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run naphtha, coker naphtha, catalytic gasoline, visbreaker naphtha, alkylate, isomate, reformat, and the like and combinations thereof.

The term "cracked-gasoline" denotes a mixture of hydrocarbons boiling in the range of from about 100°F to about 400°F, or any fraction thereof, that are products from either thermal or catalytic processes that crack larger hydrocarbon molecules into smaller molecules. Examples of suitable thermal processes include, but are not limited to, coking, thermal cracking, visbreaking and the like and combinations thereof. Examples of suitable catalytic cracking processes include, but are not limited to fluid catalytic cracking, heavy oil cracking, and the like and combinations thereof. Thus, examples of suitable cracked-gasoline include, but are not limited to, coker gasoline, thermally cracked gasoline, visbreaker gasoline, fluid catalytically cracked gasoline, heavy oil cracked gasoline, and the like and combinations thereof. In some instances, the cracked-gasoline may be fractionated and/or hydrotreated prior to desulfurization when used as a hydrocarbon-containing fluid in a process of the present invention.

The term "diesel fuel" denotes a mixture of hydrocarbons boiling in the range of from about 300°F to about 750°F, or any fraction thereof. Examples of suitable diesel fuels include, but are not limited to, light cycle oil, kerosene, jet fuel, straight-run diesel, hydrotreated diesel, and the like and combinations thereof.

The term "sulfur" denotes sulfur in any form such as elemental sulfur or a sulfur compound normally present in a hydrocarbon-containing fluid such as cracked gasoline or diesel fuel. Examples of sulfur which can be present during a process of the present invention, usually contained in a hydrocarbon-containing fluid, include, but are not limited to, hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS₂), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, substituted thiophenes, organic trisulfides, organic tetrasulfides, benzothiophene, alkyl thiophenes, alkyl benzothiophenes, alkyl dibenzothiophenes, and the like and combinations thereof as well as the heavier molecular weights of same which are normally present in a diesel fuel of the types contemplated for use in a process of the present invention, wherein each R can be an alkyl or cycloalkyl or aryl group containing one carbon atom to ten carbon atoms.

The term "fluid" denotes gas, liquid, vapor, and combinations thereof.

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The term "gaseous" denotes that state in which the hydrocarbon-containing fluid, such as cracked-gasoline or diesel fuel, is primarily in a gas or vapor phase.

The term "attrition resistance" denotes the attrition resistance of a sorbent composition of the present invention measured as the Davison Index. The term "Davison Index" (DI) refers to a measure of a sorbent's resistance to particle size reduction under controlled conditions of turbulent motion. The Davison Index represents the weight percent of the over 20 micrometer particle size fraction which is reduced to particle sizes of less than 20 micrometers under test conditions. The Davison Index is measured using a Jet cup attrition determination method. The Jet cup attrition determination method involves screening a 5 gram sample of sorbent to remove particles in the 0 to 20 micrometer size range. The particles above 20 micrometers are then subjected to a tangential jet of air at a rate of 21 liters per minute introduced through a 0.0625 inch orifice fixed at the bottom of a specially designed Jet cup (1" I.D. X 2" height) for a period of 1 hour. The Davison Index (DI) is calculated as follows:

$$DI = \frac{\text{Weight of 0 to 20 micrometer material formed during test}}{\text{Weight of original 20+ micrometer fraction being tested}} \times 100 \times \text{correction factor}$$

Correction factor (presently 0.3) is determined by using a known calibration standard to adjust for differences in jet cup dimensions and wear.

A sorbent composition of the present invention having an attrition-resistance-enhancing amount of an attrition-resistance-enhancing component has a Davison Index value generally less than about 30. Preferably, the sorbent composition has a Davison Index value in the range of from about 1 to about 25. More preferably, the sorbent composition has a Davison Index value in the range of from 5 to 20.

A sorbent composition of the present invention comprising an attrition-resistance-enhancing component has an enhanced attrition resistance when compared to sorbent compositions which do not have such attrition-resistance-enhancing component.

The term "support component" denotes any component or combination of components which can be used as a support for a sorbent composition of the present invention to help promote a desulfurization process of the present invention. Examples of a suitable support component include, but are not limited to, zinc oxide and any suitable inorganic and organic carriers and the like and combinations thereof. Examples of

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suitable inorganic carriers include, but are not limited to, silica, silica gel, alumina, diatomaceous earth, expanded perlite, kieselguhr, silica-alumina, titania, zirconia, zinc aluminate, zinc titanate, zinc silicate, magnesium aluminate, magnesium titanate, synthetic zeolites, natural zeolites, and the like and combinations thereof. Examples of
5 suitable organic carriers include, but are not limited to, activated carbon, coke, charcoal, carbon-containing molecular sieves, and the like and combinations thereof. A preferred support component comprises zinc oxide, silica, and alumina.

The term "promoter component" denotes any component which can be added to a sorbent composition of the present invention to help promote a desulfurization process of
10 the present invention. Examples of suitable promoter components include, but are not limited to, metals, metal oxides, and the like and combinations thereof.

The term "metal" denotes metal in any form such as elemental metal or a metal-containing compound.

The term "metal oxide" denotes metal oxide in any form such as a metal oxide or a
15 metal oxide precursor.

The term "attrition-resistance-enhancing component" denotes any component which can be added to a sorbent composition of the present invention to enhance the attrition resistance of such sorbent composition compared to a sorbent composition which does not contain such attrition-resistance-enhancing component. Examples of a suitable
20 attrition-resistance-enhancing component include, but are not limited to, clays, high alumina cements, natural cements, portland cement, calcium aluminate, calcium silicate, talc, and the like and combinations thereof. The term "clay" denotes any clay which can be used as an attrition-resistance-enhancing component of a sorbent composition of the present invention. Examples of a suitable clay include, but are not limited to, bentonite,
25 sodium bentonite, acid-washed bentonite, atapulgite, china clay, kaolinite, montmorillonite, illite, halloysite, hectonite, sepiolite, and the like and combinations thereof. Preferably, such attrition-resistance-enhancing component comprises a clay. More preferably, such attrition-resistance-enhancing component is selected from the group consisting of bentonite, sodium bentonite, acid-washed bentonite, and the like and
30 combinations thereof. Most preferably, such attrition-resistance-enhancing component is bentonite.

During the preparation of a sorbent composition of the present invention, the promoter component selected from the group consisting of metals, metal oxides, and the like and combinations thereof may initially be in the form of a metal-containing compound(s) and/or a metal oxide precursor(s). It should be understood that when the
5 promoter component is initially a metal-containing compound(s) and/or a metal oxide precursor(s), a portion of, or all of, such compound(s) and/or precursor(s) may be converted to the corresponding metal or metal oxide of such compound(s) and/or precursor(s) during the inventive process(es) disclosed herein.

The term "reduced-valence promoter component" denotes that a substantial
10 portion of the valence of such promoter component is reduced, preferably to a value of zero.

When an attrition-resistance-enhancing component is distributed throughout a particulate composition, comprising a support component, preferably such support component comprises zinc oxide, silica, and alumina, and a promoter component, there is
15 provided a novel sorbent composition of the present invention which permits the removal of sulfur from a hydrocarbon-containing fluid, such as cracked-gasoline or diesel fuel, without having a significant adverse effect on the olefin content of such treated hydrocarbon-containing fluid, thus avoiding a significant reduction in octane values of such treated hydrocarbon-containing fluid. Moreover, the use of a novel sorbent
20 composition of the present invention results in a significant reduction of the sulfur content of the treated hydrocarbon-containing fluid. Further, a novel sorbent composition of the present invention has an enhanced attrition resistance when compared to a sorbent composition which does not have such attrition-resistance-enhancing component.

When a support component generally comprising zinc oxide and any inorganic or
25 organic carrier, preferably comprising zinc oxide, silica and alumina, is used, the zinc oxide used in the preparation of a sorbent composition of the present invention can be either in a form of zinc oxide such as powdered zinc oxide, or in the form of one or more zinc compounds that are convertible to zinc oxide under the conditions of preparation described herein. Examples of suitable zinc compounds include, but are not limited to,
30 zinc sulfide, zinc sulfate, zinc hydroxide, zinc carbonate, zinc acetate, zinc nitrate, and the like and combinations thereof. Preferably, the zinc oxide is in the form of powdered zinc

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oxide.

When a preferred support component comprising zinc oxide, silica, and alumina is used, the silica used in the preparation of a sorbent composition of the present invention can be either in the form of silica or in the form of one or more silicon compounds. Any
5 suitable type of silica may be employed in preparing a sorbent composition of the present invention. Examples of suitable types of silica include, but are not limited to, diatomite, expanded perlite, silicalite, silica colloid, flame-hydrolyzed silica, hydrolyzed silica, silica gel, precipitated silica and the like and combinations thereof. In addition, silicon
10 compounds that are convertible to silica such as silicic acid, ammonium silicate and the like and combinations thereof can also be employed. Preferably, the silica is in the form of diatomite or expanded perlite.

When a preferred support component comprising zinc oxide, silica, and alumina is used, the alumina used in preparing a sorbent composition of the present invention can be present in the source of silica, can be any suitable commercially available alumina
15 material (including, but not limited to, colloidal alumina solutions, hydrated aluminas, and, generally, those alumina compounds produced by the dehydration of alumina hydrates), or both. The preferred alumina is a hydrated alumina such as, but not limited to, boehmite or pseudoboehmite.

The promoter component used in preparing a sorbent composition of the present
20 invention can be any metal, metal oxide, and the like and combinations thereof in any form which is effective in desulfurizing a hydrocarbon-containing fluid according to a process of the present invention. Generally such promoter component is selected from the group consisting of metals, metal oxides, and the like and combinations thereof including
25 compounds which contain such metals and metal oxides. Examples of suitable metals include, but are not limited to, cobalt, nickel, iron, manganese, copper, zinc, molybdenum, tungsten, silver, tin, vanadium, antimony, and the like and combinations thereof. Examples of suitable metal oxides include, but are not limited to, cobalt oxides, nickel oxides, iron oxides, manganese oxides, copper oxides, zinc oxides, molybdenum
30 oxides, tungsten oxides, silver oxides, tin oxides, vanadium oxides, antimony oxides, and the like and combinations thereof. Generally such metals are contained in metal-containing compounds which can be used to incorporate the metal of such metal-

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containing compounds on, in, or with a dried and calcined particulate material to thereby form a dried and calcined promoted particulate material which can then be further dried and calcined, and preferably reduced, to thereby form a sorbent composition of the present invention.

5 Some examples of the form which such metals can be in include, but are not limited to, metal acetates, metal carbonates, metal nitrates, metal sulfates, metal thiocyanates, and the like and combinations thereof. Preferably, the promoter component is selected from the group consisting of nickel, cobalt, and the like and combinations thereof. More preferably, the promoter component is nickel. In a preferred method of
10 making process of the present invention, the sorbent composition is promoted with a precursor of a nickel oxide such as nickel nitrate, more preferably nickel nitrate hexahydrate.

 When the support component comprises zinc oxide and any inorganic or organic carrier, preferably comprising zinc oxide, silica and alumina, the zinc oxide will generally
15 be present in a sorbent composition of the present invention in an amount in the range of from about 10 to about 90 weight percent zinc oxide based on the total weight of the sorbent composition, preferably in an amount in the range of from about 15 to about 60 weight percent zinc oxide and, more preferably, in an amount in the range of from 20 to 55 weight percent zinc oxide.

20 When the support component comprises a preferred support component comprising zinc oxide, silica, and alumina, the silica will generally be present in a sorbent composition of the present invention in an amount in the range of from about 5 to about 85 weight percent silica based on the total weight of the sorbent composition, preferably in an amount in the range of from about 10 to about 60 weight percent silica and, more
25 preferably, in an amount in the range of from 15 to 55 weight percent silica.

 When the support component comprises a preferred support component comprising zinc oxide, silica, and alumina, the alumina will generally be present in a sorbent composition of the present invention in an amount in the range of from about 0.1 to about 30 weight percent alumina based on the total weight of the sorbent composition,
30 preferably in an amount in the range of from about 1 to about 20 weight percent alumina and, more preferably, in an amount in the range of from 5 to 15 weight percent alumina.

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The attrition-resistance-enhancing component will generally be present in an attrition-resistance-enhancing amount which is effective in providing a sorbent composition of the present invention having an enhanced attrition resistance compared to a sorbent composition which does not have such attrition-resistance-enhancing component. The attrition-resistance-enhancing component will generally be present in a sorbent composition of the present invention in an amount in the range of from about 1 to about 30 weight percent attrition-resistance-enhancing component based on the total weight of the sorbent composition, preferably in an amount in the range of from about 5 to about 20 weight percent attrition-resistance-enhancing component and, more preferably, in an amount in the range of from 5 to 15 weight percent attrition-resistance-enhancing component.

The promoter component will generally be present in a sorbent composition of the present invention in an amount in the range of from about 5 to about 50 weight percent promoter component based on the total weight of the sorbent composition, preferably in an amount in the range of from about 8 to about 45 weight percent promoter component and, more preferably, in an amount in the range of from 10 to 40 weight percent promoter component. When the promoter component comprises a combination of metals, metal oxides, and the like, such as a preferred bimetallic promoter component, the bimetallic promoter component should comprise a weight ratio of the two metals forming such bimetallic promoter component in the range of from about 20:1 to about 1:20. In a preferred embodiment of the present invention, the promoter component is a bimetallic promoter component comprising nickel and cobalt in a weight ratio of about 1:1.

In the manufacture of a sorbent composition of the present invention, the support component is generally prepared by combining the support component, generally comprising zinc oxide and any inorganic or organic carrier, preferably comprising zinc oxide, silica and alumina, and the attrition-resistance-enhancing component together in appropriate proportions by any suitable method or manner which provides for the intimate mixing of such components to thereby provide a substantially homogeneous mixture comprising zinc oxide, any inorganic or organic carrier, and an attrition-resistance-enhancing component, preferably a substantially homogeneous mixture comprising zinc oxide, silica, alumina, and an attrition-resistance-enhancing component. Any suitable

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means for mixing the support component, preferably comprising zinc oxide, silica, and alumina, and the attrition-resistance-enhancing component can be used to achieve the desired dispersion of such components. Examples of suitable means for mixing include, but are not limited to, mixing tumblers, stationary shells or troughs, Muller mixers, which
5 are of the batch or continuous type, impact mixers, and the like. It is presently preferred to use a Muller mixer as the means for mixing the support component, preferably comprising zinc oxide, silica, alumina, and the attrition-resistance-enhancing component.

The support component, generally comprising zinc oxide and any inorganic or organic carrier, preferably comprising zinc oxide, silica and alumina, and the attrition-
10 resistance-enhancing component, preferably comprising a clay, are contacted together by any manner known in the art to provide a resulting mixture which can be in a form selected from the group consisting of a wet mix, a dough, a paste, a slurry and the like. Such resulting mixture can then be shaped to form a particulate(s) selected from the group consisting of a granulate, an extrudate, a tablet, a sphere, a pellet, a micro-sphere, and the
15 like. For example, if the resulting mixture is in the form of a wet mix, the wet mix can be densified, dried under a drying condition as disclosed herein, calcined under a calcining condition as disclosed herein, and thereafter shaped, or particulated, through the granulation of the densified, dried, calcined mix to form granulates. Also for example, when the resulting mixture of the support component, generally comprising zinc oxide
20 and any inorganic or organic carrier, preferably comprising zinc oxide, silica and alumina, and the attrition-resistance-enhancing component, preferably comprising a clay, is in the form of either a dough state or paste state, such resulting mixture can then be shaped, preferably extruded, to form a particulate, preferably cylindrical extrudates having a diameter in the range of from about 1/32 inch to 1/2 inch and any suitable length,
25 preferably a length in the range of from about 1/8 inch to about 1 inch. The resulting particulates, preferably cylindrical extrudates, are then dried under a drying condition as disclosed herein and then calcined under a calcining condition as disclosed herein.

More preferably, the resulting mixture of the support component, preferably comprising zinc oxide, silica and alumina, and the attrition-resistance-enhancing
30 component, preferably comprising a clay, is in the form of a slurry and the particulation of such slurry is achieved by spray drying the slurry to form micro-spheres thereof having a

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size generally in the range of from about 1 micrometer to about 1000 micrometers, preferably in the range of from about 5 micrometers to about 500 micrometers. Such micro-spheres are then subjected to drying under a drying condition as disclosed herein and calcining under a calcining condition as disclosed herein.

- 5 When the particulation is achieved by preferably spray drying, a dispersant component can be utilized and can be any suitable compound that helps to promote the spray drying ability of the resulting mixture which is preferably in the form of a slurry. In particular, these dispersant components are useful in preventing deposition, precipitation, settling, agglomerating, adhering, and caking of solid particles in a fluid medium.
- 10 Examples of suitable dispersant components include, but are not limited to, condensed phosphates, sulfonated polymers, ammonium polyacrylate, sodium polyacrylate, ammonium polymethacrylate, sodium polymethacrylate, poly(methyl methacrylate), poly(acrylic acid, sodium salt), polyacrylamide, and the like and combinations thereof. The term condensed phosphates refers to any dehydrated phosphate where the $H_2O:P_2O_5$,
15 is less than about 3:1. Additional examples of suitable dispersant components include, but are not limited to, sodium pyrophosphate, sodium metaphosphate, sulfonated styrene maleic anhydride polymer, and the like and combinations thereof. The amount of a dispersant component used is generally in the range of from about 0.01 weight percent dispersant component based on the total weight of the components to about 10 weight
20 percent dispersant component. Preferably, the amount of a dispersant component used is generally in the range of from about 0.1 weight percent to about 8 weight percent and, more preferably, the amount of a dispersant component used is in the range of from 1 weight percent to 5 weight percent.

- In preparing a spray-dried sorbent composition of the present invention, an acid
25 component can be used. In general, the acid component can be an organic acid or a mineral acid. If the acid component is an organic acid, it is preferred if it is a carboxylic acid. If the acid component is a mineral acid it is preferred if it is a mineral acid selected from the group consisting of nitric acid, phosphoric acid, hydrochloric acid, sulfuric acid, and the like and combinations thereof. Generally, the acid is used with water to form a
30 dilute aqueous acid solution. The amount of acid in the acid component is generally in the range of from about 0.01 volume percent based on the total volume of the acid

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component to about 20 volume percent. Preferably, the amount of acid is in the range of from about 0.1 volume percent to about 15 volume percent and, more preferably, the amount of acid is in the range of from 1 volume percent to 10 volume percent. In general, the amount of acid component to be used is based on the amount of the dry components.

5 That is, the ratio of all the dry components (in grams) to the acid component (in milliliters) should be less than about 1.75:1. However, it is preferred if this ratio is less than about 1.25:1 and it is more preferred if it is less than about 1:1. These ratios will help to form a mixture that is a liquid solution, a slurry, or a paste that is capable of being dispersed in a fluid-like spray.

10 In preparing a preferred spray-dried sorbent composition of the present invention, a support component, comprising zinc oxide, silica, and alumina, a dispersant component, and an attrition-resistance-enhancing component comprising a clay can be contacted together in any manner known in the art that will form a mixture that is a liquid solution, a slurry, or a paste that is capable of being dispersed in a fluid-like spray. When a support
15 component, a dispersant component, and an attrition-resistance-enhancing component are solids, then they should be contacted in a liquid medium to form a mixture that is a liquid solution, a slurry, or a paste that is capable of being dispersed in a fluid-like spray. Suitable means for contacting these components are known in the art such as, for example, tumblers, stationary shells, troughs, muller mixers, impact mixers, and the like.

20 Generally, these components, after contacting to form a mixture, are contacted with an acid component as described herein. However, the dry components and the acid component(s) can be contacted together simultaneously or separately.

After the components are contacted together to form a mixture, they are subjected to spray drying to form a spray-dried sorbent material comprising particulates, preferably
25 in the form of micro-spheres, that have a mean particle size in the ranges as disclosed herein. Spray drying is known in the art and is discussed in *Perry's Chemical Engineers' Handbook*, Sixth Edition, published by McGraw-Hill, Inc., at pages 20-54 through 20-58. Additional information can be obtained from the *Handbook of Industrial Drying*, published by Marcel Dekker, Inc., at pages 243 through 293.

30 The spray-dried sorbent material can then be dried under a drying condition as disclosed herein and then calcined, preferably in an oxidizing atmosphere such as in the

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presence of oxygen or air, under a calcining condition as disclosed herein to form a calcined, spray-dried sorbent material. The calcination can be conducted under any suitable condition that removes residual water and oxidizes any combustibles.

Generally, the spray-dried sorbent material has a mean particle size in the range of
5 from about 1 micrometer to about 1000 micrometers, preferably in the range of from about 5 micrometers to about 500 micrometers and, more preferably, in the range of from 10 micrometers to 200 micrometers.

The term "mean particle size" refers to the size of the particulate material as determined by using a RO-TAP Testing Sieve Shaker, manufactured by W.S. Tyler Inc.,
10 of Mentor, Ohio, or other comparable sieves. The material to be measured is placed in the top of a nest of standard eight inch diameter stainless steel frame sieves with a pan on the bottom. The material undergoes sifting for a period of about 10 minutes; thereafter, the material retained on each sieve is weighed. The percent retained on each sieve is calculated by dividing the weight of the material retained on a particular sieve by the
15 weight of the original sample. This information is used to compute the mean particle size.

The resulting particulated (preferably spray-dried), dried, and calcined material comprising a support component (generally comprising zinc oxide and any inorganic or organic carrier, preferably comprising zinc oxide, silica, and alumina) and an attrition-
20 resistance-enhancing component (preferably comprising a clay) are then incorporated with a promoter component selected from the group consisting of metals, metal oxides, and the like and combinations thereof including compounds containing such metals and metal oxides, preferably a nickel oxide compound or a nickel oxide precursor or a bimetallic promoter component comprising a nickel oxide compound, or a nickel oxide precursor,
25 and a cobalt oxide compound or a cobalt oxide precursor.

Following the incorporating of the particulated, dried, and calcined material, comprising a support component and an attrition-resistance-enhancing component, with a promoter component, the resulting promoted particulates are then subjected to drying under a drying condition as disclosed herein and calcined under a calcining condition as
30 disclosed herein to thereby provide dried, calcined, promoted particulates prior to the subjecting of such dried, calcined, promoted particulates to reduction with a reducing

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agent, preferably hydrogen.

The promoter component(s) may be incorporated on, in, or with the particulated (preferably spray-dried), dried, and calcined material comprising a support component and an attrition-resistance-enhancing component by any suitable means or method for incorporating the promoter component(s) on, in, or with, a substrate material, such as the dried and calcined particulates, which results in the formation of a promoted sorbent composition which can then be dried under a drying condition as disclosed herein and calcined under a calcining condition as disclosed herein to thereby provide dried, calcined, promoted particulates. The dried, calcined, promoted particulates can then be subjected to reduction with a reducing agent, preferably hydrogen, to thereby provide a sorbent composition of the present invention. Examples of means or methods for incorporating a promoter component(s) include, but are not limited to, impregnating, soaking, spraying, and the like and combinations thereof.

A preferred method of incorporating is impregnating using any standard incipient wetness impregnation technique (i.e., essentially completely filling the pores of a substrate material with a solution of the incorporating elements) for impregnating a substrate, such as the preferred particulated, dried, and calcined material (i.e., particulates) comprising a support component (preferably comprising zinc oxide, silica and alumina) and an attrition-resistance-enhancing component (preferably comprising a clay) prepared according to a process of the present invention, with a promoter component(s). A preferred method uses an impregnating solution comprising the desirable concentration of a promoter component(s) so as to ultimately provide a promoted particulate(s) which can then be subjected to drying under a drying condition as disclosed herein and calcining under a calcining condition as disclosed herein followed by reduction with a reducing agent such as hydrogen to provide a sorbent composition of the present invention. The impregnating solution can be any aqueous solution and amounts of such solution which suitably provides for the impregnation of the particulates comprising a support component (preferably comprising zinc oxide, silica and alumina) and an attrition-resistance-enhancing component (preferably comprising a clay) prepared according to a process of the present invention to give an amount of promoter component that provides, after reduction with a reducing agent, a reduced promoter component

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content sufficient to permit the removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel when such fluid is treated in accordance with a process of the present invention.

It can be desirable to use an impregnating solution comprising a promoter
5 component and an aqueous or nonaqueous solvent for the impregnation of the
particulates. A preferred impregnating solution comprises an aqueous solution formed by
dissolving a metal-containing compound, preferably such metal-containing compound is
in the form of a metal salt, such as, but not limited to, a metal chloride, a metal nitrate, a
metal sulfate, and the like and combinations thereof, in an aqueous solvent comprising
10 water. Examples of suitable aqueous and nonaqueous solvents include, but are not
limited to, water, alcohols, esters, ethers, ketones, and the like and combinations thereof.

Generally, the weight ratio of promoter component to the aqueous or nonaqueous
solvent of such impregnating solution can be in the range of from about 1:1 to about 4:1,
preferably, in the range of from 1.5:1 to 3:1.

15 In preparing the spray-dried sorbent material, a promoter component(s) can be
added to the spray-dried sorbent material as a component(s) of the original mixture, or
can be added after the original mixture has been spray dried, dried, and calcined. If a
promoter component(s) is added to the spray-dried sorbent material after it has been
spray-dried, dried, and calcined, the spray-dried sorbent material should be dried again
20 under a drying condition as disclosed herein and then calcined again under a calcining
condition as disclosed herein.

A preferred impregnating solution is formed by dissolving a metal-containing
compound (such as nickel nitrate hexahydrate) in water. It is acceptable to use somewhat
of an acidic solution to aid in the dissolution of the metal-containing compound. It is
25 more preferred for the particulates to be impregnated with a nickel component by use of a
solution containing nickel nitrate hexahydrate dissolved in water.

An example method of incorporating a promoter component on, in, or with a
material comprising a support component and an attrition-resistance-enhancing
component, preferably particulates comprising zinc oxide, silica, alumina, and a clay,
30 prepared according to a process of the present invention, is to impregnate such
particulates with a promoter component, initially in the form of a metal-containing

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compound, which has been melted under a melting condition as described herein. Preferably such promoter component is initially in the form of a metal-containing compound such as a metal salt, such as, but not limited to, a metal chloride, a metal nitrate, a metal sulfate, and the like and combinations thereof (such as, but not limited to, 5 nickel nitrate hexahydrate). Addition of small amounts of an aqueous or nonaqueous solvent, such as water, to the promoter component can be used to assist in the melting of such promoter component, but such use of a solvent is not required.

Such melting condition includes a temperature in a range of from the melting point of the promoter component to below the decomposition temperature of the promoter 10 component for a time period and at a pressure that provides for a melted promoter component. The term "decomposition temperature" refers to the temperature at which the promoter component is no longer soluble and is no longer suitable for incorporating, preferably impregnating, the promoter component onto the material comprising a support component and an attrition-resistance-enhancing component according to a process of the 15 present invention.

The temperature of such melting condition varies depending on the promoter component but such temperature should be such as to provide a melted promoter component. Such temperature is generally in the range of from about 75°F to about 700°F, preferably in the range of from about 85°F to about 300°F, more preferably in the 20 range of from about 95°F to about 280°F and, most preferably, in the range of from 95°F to 250°F.

Such melting condition can include a time period generally in the range of from about 1 minute to about 2 hours, preferably in the range of from about 5 minutes to about 1.5 hours and, most preferably, in the range of from 5 minutes to 1 hour. Such melting 25 condition can include a pressure generally in the range of from about atmospheric (i.e., about 14.7 pounds per square inch absolute) to about 150 pounds per square inch absolute (psia), preferably in the range of from about atmospheric to about 100 psia, most preferably about atmospheric, so long as the desired temperature can be maintained.

The thus-melted promoter component is then used to incorporate, preferably 30 impregnate, such promoter component onto a material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc

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oxide, silica, alumina, and a clay, prepared according to a process of the present invention. The melted promoter component is incorporated, preferably impregnated, onto the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, by any manner or method which results in substantially all the surface area of the particulates being contacted with the melted promoter component resulting in distribution of the promoter component. The phrase "substantially all the surface area of the particulates being contacted with the melted promoter component" generally refers to greater than twenty-five percent of the surface area of the particulates, preferably greater than forty percent of the surface area of the particulates, more preferably greater than sixty percent of the surface area of the particulates, and most preferably greater than ninety-five percent of the surface area of the particulates being contacted with the melted promoter component.

Another example method of incorporating, preferably impregnating, a melted promoter component onto the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, is by mixing a solid promoter component (i.e., an unmelted promoter component) with the particulates by any manner or method which results in a mixture of particulates and solid promoter component. The mixture of particulates and solid promoter component is then subjected to a melting condition as described herein, preferably while such mixture is subjected to constant stirring or tumbling, which results in substantially all the surface area of the particulates being contacted with a melted promoter component resulting in distribution of the promoter component.

Another example method of incorporating, preferably impregnating, a melted promoter component onto the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, is by pre-heating the particulates under a heating condition as described herein to thereby provide a pre-heated support component (i.e., pre-heated particulates) followed by contact with a solid promoter component (i.e., an unmelted promoter component) which results in a

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melting of the solid promoter component upon contact with the pre-heated particulates which further results in substantially all the surface area of the particulates being contacted with the melted promoter component. Preferably such pre-heated particulates are under constant stirring or tumbling during contact with the promoter component.

5 Such mixture of particulates and melted promoter component can be further heated near the melting point of the promoter component for a time period in the range of from about 0.5 hour to about 15 hours, preferably in the range of from about 1 hour to about 8 hours and, most preferably, in the range of from 1 hour to 5 hours to further aid in the melting of the promoter component.

10 Such heating condition, suitable for pre-heating the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, can include a temperature generally in the range of from about 175°F to about 300°F, preferably in the range of from about 185°F to about 280°F and, more
15 preferably, in the range of from 190°F to 260°F. Such heating condition can include a time period generally in the range of from about 1 minute to about 2 hours, preferably in the range of from about 5 minutes to about 1.5 hours and, more preferably, in the range of from 5 minutes to 1 hour. Such heating condition can include a pressure generally in the range of from about atmospheric (i.e., about 14.7 pounds per square inch absolute) to
20 about 150 pounds per square inch absolute (psia), preferably in the range of from about atmospheric to about 100 psia, more preferably about atmospheric, so long as the desired temperature can be maintained.

Another example method of incorporating, preferably impregnating, a melted promoter component onto the material comprising a support component and an attrition-
25 resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, is by subjecting a solid promoter component to a melting condition as described herein to thereby provide a melted promoter component which has become viscous enough to pour. The particulates are then contacted with such melted promoter component by pouring
30 such melted promoter component onto the surface of the particulates by any manner or method(s) which results in substantially all the surface area of the particulates being

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contacted with the melted promoter component resulting in distribution of the promoter component. Preferably, such melted promoter component is poured onto the surface of the particulates while such particulates are under constant stirring or tumbling. It can be desirable to pre-heat the material comprising a support component and an attrition-
5 resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, under a heating condition as described herein before contact with the melted promoter component.

In another example method, solid nickel nitrate hexahydrate is used to incorporate,
10 preferably impregnate, the nickel of such solid nickel nitrate hexahydrate onto the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention. The nickel of such solid nickel nitrate hexahydrate is incorporated, preferably impregnated, onto the particulates by
15 mixing such solid nickel nitrate hexahydrate with the particulates by any manner or method which results in a mixture of solid nickel nitrate hexahydrate and particulates and then subjecting such mixture, while under constant stirring or tumbling, to a melting condition as described herein with results in substantially all the surface area of the particulates being contacted with melted nickel nitrate hexahydrate resulting in
20 distribution of the nickel nitrate hexahydrate. In addition, cobalt nitrate hexahydrate or iron nitrate nonahydrate or manganese nitrate hexahydrate or copper nitrate or zinc nitrate hexahydrate or silver nitrate or the like and combinations thereof can be used in place of nickel nitrate hexahydrate to incorporate, preferably impregnate, the metal of such metal-containing compound(s) onto the particulates in the same above-described manner as for
25 incorporating, preferably impregnating, the nickel of such nickel nitrate hexahydrate. Also preferred, solid nickel nitrate hexahydrate and solid cobalt nitrate hexahydrate are mixed with the particulates and then the resulting mixture, while under constant stirring or tumbling, is subjected to a melting condition as described herein to incorporate, preferably impregnate, the nickel and cobalt onto the particulates. After drying and
30 calcining, a sorbent composition comprising a bimetallic promoter component comprising nickel and cobalt is formed.

In another example method, the nickel of such solid nickel nitrate hexahydrate is incorporated, preferably impregnated, onto the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, by contacting such particulates, which have been pre-heated under a heating condition as described herein, with the solid nickel nitrate hexahydrate while under constant stirring or tumbling. Such contacting results in a melting of the solid nickel nitrate hexahydrate upon contact with the pre-heated particulates which results in substantially all the surface area of the pre-heated particulates being contacted with melted nickel nitrate hexahydrate resulting in distribution of the nickel nitrate hexahydrate. In addition, cobalt nitrate hexahydrate or iron nitrate nonahydrate or manganese nitrate hexahydrate or copper nitrate or zinc nitrate hexahydrate or silver nitrate or the like and combinations thereof can be used in place of nickel nitrate hexahydrate to incorporate, preferably impregnate, the metal of such metal-containing compound(s) onto the pre-heated particulates in the same above-described manner as for incorporating, preferably impregnating, the nickel of such nickel nitrate hexahydrate. Also, solid nickel nitrate hexahydrate and solid cobalt nitrate hexahydrate can be contacted with the pre-heated particulates while under constant stirring or tumbling to incorporate, preferably impregnate, the nickel and cobalt onto the particulates. After drying and calcining, a sorbent composition comprising a bimetallic promoter component comprising nickel and cobalt is formed.

In another example method, solid nickel nitrate hexahydrate is subjected to a melting condition to thereby provide a melted nickel nitrate hexahydrate which is viscous enough to pour. The resulting melted nickel nitrate hexahydrate is then used to incorporate, preferably impregnate, the nickel of such melted nickel nitrate hexahydrate onto the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay, prepared according to a process of the present invention, which have been pre-heated under a heating condition as described herein. The nickel of such melted nickel nitrate hexahydrate is incorporated, preferably impregnated, onto the pre-heated particulates by adding such melted nickel nitrate hexahydrate to the pre-heated particulates by pouring

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such melted nickel nitrate hexahydrate onto the surface of the pre-heated particulates by any manner or method which results in substantially all the surface area of the particulates being contacted with the melted nickel nitrate hexahydrate resulting in distribution of the nickel nitrate hexahydrate. Preferably, such melted nickel nitrate hexahydrate is poured
5 onto the surface of the pre-heated particulates while such particulates are under constant stirring or tumbling. In addition, cobalt nitrate hexahydrate or iron nitrate nonahydrate or manganese nitrate hexahydrate or copper nitrate or zinc nitrate hexahydrate or silver nitrate or the like and combinations thereof can be used in place of nickel nitrate hexahydrate to incorporate, preferably impregnate, the metal of such metal-containing
10 compound(s) onto the pre-heated particulates in the same above-described manner as for incorporating, preferably impregnating, the nickel of such nickel nitrate hexahydrate. Also, melted nickel nitrate hexahydrate and melted cobalt nitrate hexahydrate can be poured onto the surface of the pre-heated particulates while such particulates are under constant stirring or tumbling. After drying and calcining, a sorbent composition
15 comprising a bimetallic promoter component comprising nickel and cobalt is formed.

Generally, the amount of a promoter component(s) incorporated, preferably impregnated, onto, into, or with the material comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina and a clay, prepared according to a process of the present invention, is an
20 amount which provides, after the promoted particulate material has been dried under a drying condition as disclosed herein and calcined under a calcining condition as disclosed herein, a sorbent composition having an amount of promoter component as disclosed herein.

Generally, a drying condition, as referred to herein, can include a temperature in
25 the range of from about 180°F to about 290°F, preferably in the range of from about 190°F to about 280°F and, more preferably, in the range of from 200°F to 270°F. Such drying condition can also include a time period generally in the range of from about 0.5 hour to about 60 hours, preferably in the range of from about 1 hour to about 40 hours and, more preferably, in the range of from 1.5 hours to 20 hours. Such drying condition
30 can also include a pressure generally in the range of from about atmospheric (i.e., about 14.7 pounds per square inch absolute) to about 150 pounds per square inch absolute

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(psia), preferably in the range of from about atmospheric to about 100 psia, more preferably about atmospheric, so long as the desired temperature can be maintained. Any drying method(s) known to one skilled in the art such as, for example, air drying, heat drying, vacuum drying, and the like and combinations thereof can be used.

5 Generally, a calcining condition, as referred to herein, can include a temperature in the range of from about 400°F to about 1800°F, preferably in the range of from about 600°F to about 1600°F and, more preferably, in the range of from 800°F to about 1500°F. Such calcining condition can also include a time period generally in the range of from about 1 hour to about 60 hours, preferably in the range of from about 2 hours to about 20
10 hours and, more preferably, in the range of from 3 hours to 15 hours. Such calcining condition can also include a pressure, generally in the range of from about 7 pounds per square inch absolute (psia) to about 750 psia, preferably in the range of from about 7 psia to about 450 psia and, more preferably, in the range of from 7 psia to 150 psia.

 Once a promoter component has been incorporated on, in, or with the material
15 comprising a support component and an attrition-resistance-enhancing component, preferably particulates comprising zinc oxide, silica, alumina, and a clay (preferably bentonite), the desired reduced-valence promoter component sorbent, preferably reduced-valence nickel sorbent, is prepared by drying the resulting composition under a drying
20 condition as disclosed herein followed by calcining under a calcining condition as disclosed herein to thereby provide a dried, calcined, promoted particulate(s). The dried, calcined, promoted particulates are thereafter subjected to reduction with a suitable reducing agent, preferably hydrogen, to thereby provide a composition comprising a reduced-valence promoter component, preferably a zero-valence promoter component, with such zero-valence promoter component, preferably zero-valence nickel, being
25 present in an amount sufficient to permit the removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel, according to a process of the present invention.

 A sorbent composition of the present invention comprising a reduced-valence promoter component is a composition that has the ability to react chemically and/or
30 physically with sulfur. It is also preferable that the sorbent composition removes diolefins and other gum-forming compounds from cracked-gasoline.

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A sorbent composition of the present invention comprising a reduced-valence promoter component comprises a promoter component, preferably comprising nickel, that is in a substantially reduced valence state, preferably a zero valence state. Preferably, the reduced-valence promoter component is reduced nickel. The amount of reduced-valence promoter component, preferably reduced nickel, in a sorbent composition of the present invention is an amount which will permit the removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel. Such amount of reduced-valence promoter component, preferably reduced nickel, in a sorbent composition of the present invention is generally in the range of from about 5 to about 50 weight percent of the total weight of the sorbent composition. Preferably the reduced-valence promoter component, preferably reduced nickel, is present in an amount in the range of from about 8 to about 45 weight percent of the total weight of the sorbent composition and, more preferably, in an amount in the range of from 10 to 40 weight percent of the total weight of the sorbent composition.

In one presently preferred embodiment of a sorbent composition of the present invention, the reduced nickel is present in an amount in the range of from 10 to 40 weight percent reduced nickel based on the total weight of the sorbent composition and the reduced nickel has been substantially reduced to zero valence.

In another presently preferred embodiment of a sorbent composition of the present invention, zinc oxide is present in an amount in the range of from about 35 to about 50 weight percent zinc oxide based on the total weight of the sorbent composition, silica is present in an amount in the range of from about 30 to about 40 weight percent silica based on the total weight of the sorbent composition, alumina is present in an amount in the range of from about 6 to about 12 weight percent alumina based on the total weight of the sorbent composition, bentonite is present in an amount in the range of from about 2 to about 12 weight percent bentonite based on the total weight of the sorbent composition, and nickel is present, prior to reduction to zero valence, in an amount in the range of from about 14 to about 30 weight percent nickel based on the total weight of the sorbent composition.

A sorbent composition of the present invention which is useful in a process of the present invention can be prepared by a process comprising:

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(a) contacting a support component, preferably comprising zinc oxide, silica, and alumina, and an attrition-resistance-enhancing component, preferably comprising a clay, so as to form a mixture selected from the group consisting of a wet mix, a dough, a paste, a slurry and the like and combinations thereof;

5 (b) particulating, preferably spray-drying, the mixture to form particulates selected from the group consisting of granulates, extrudates, tablets, pellets, spheres, micro-spheres, and the like and combinations thereof, preferably micro-spheres, where such particulates comprise such support component and such attrition-resistance-enhancing component;

10 (c) drying the particulate under a drying condition as disclosed herein to form a dried particulate;

(d) calcining the dried particulate under a calcining condition as disclosed herein to form a calcined particulate;

15 (e) incorporating, preferably impregnating, the calcined particulate with a promoter component selected from the group consisting of metal, metal oxides, and the like and combinations thereof to form a promoted particulate;

(f) drying the promoted particulate under a drying condition as disclosed herein to form a dried, promoted particulate;

20 (g) calcining the dried, promoted particulate under a calcining condition as disclosed herein to form a calcined, promoted particulate; and

(h) reducing the calcined, promoted particulate with a suitable reducing agent so as to produce a sorbent composition having a reduced-valence promoter component content therein, preferably a reduced-valence nickel content therein, and wherein the reduced-valence promoter component content is present in an amount effective for the
25 removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel when such hydrocarbon-containing fluid is contacted with a sorbent composition of the present invention according to a process of the present invention.

A process of using a novel sorbent composition(s) of the present invention to desulfurize a hydrocarbon-containing fluid comprising cracked-gasoline or diesel fuel to
30 provide a desulfurized hydrocarbon-containing fluid comprising desulfurized cracked-gasoline or desulfurized diesel fuel comprising:

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(a) desulfurizing, in a desulfurization zone, a hydrocarbon-containing fluid with a sorbent composition of the present invention to thereby provide a desulfurized hydrocarbon-containing fluid and a resulting sulfurized sorbent composition;

5 (b) separating the desulfurized hydrocarbon-containing fluid and the resulting sulfurized sorbent composition;

(c) regenerating, in a regeneration zone, at least a portion of the resulting sulfurized sorbent composition to thereby provide a regenerated, desulfurized, sorbent composition;

10 (d) activating (i.e., reducing), in an activation zone, at least a portion of the regenerated, desulfurized, sorbent composition to thereby provide an activated (i.e., reduced), regenerated, desulfurized sorbent composition; and

(e) returning at least a portion of the activated (i.e., reduced), regenerated, desulfurized sorbent composition to the desulfurization zone.

15 The desulfurizing of a hydrocarbon-containing fluid is carried out under a set of conditions that includes total pressure, temperature, weight hourly space velocity, and hydrogen flow. These conditions are such that the sorbent composition can desulfurize the hydrocarbon-containing fluid to produce a desulfurized hydrocarbon-containing fluid and a sulfurized sorbent composition.

20 In carrying out the desulfurizing of a hydrocarbon-containing fluid, it is preferred that the hydrocarbon-containing fluid, preferably cracked-gasoline or diesel fuel, be in a gas or vapor phase. However, in the practice of the present invention it is not essential that the hydrocarbon-containing fluid be totally in a gas or vapor phase.

25 In carrying out the desulfurizing of a hydrocarbon-containing fluid, the total pressure can be in the range of from about 15 pounds per square inch absolute (psia) to about 1500 psia. However, it is presently preferred that the total pressure be in a range of from about 50 psia to about 500 psia. In general, the temperature should be sufficient to keep the hydrocarbon-containing fluid in essentially a vapor or gas phase. While such temperatures can be in the range of from about 100°F to about 1000°F, it is presently preferred that the temperature be in the range of from about 400°F to about 800°F when
30 treating a cracked-gasoline and in the range of from about 500°F to about 900°F when treating a diesel fuel.

Weight hourly space velocity (WHSV) is defined as the numerical ratio of the rate at which a hydrocarbon-containing fluid is charged to the desulfurization zone in pounds per hour at standard condition of temperature and pressure (STP) divided by the pounds of sorbent composition contained in the desulfurization zone to which the hydrocarbon-containing fluid is charged. In the practice of the present invention, such WHSV should be in the range of from about 0.5 hr^{-1} to about 50 hr^{-1} , preferably in the range of from about 1 hr^{-1} to about 20 hr^{-1} . The desulfurizing (i.e., desulfurization) of a hydrocarbon-containing fluid should be conducted for a time sufficient to effect the removal of sulfur from such hydrocarbon-containing fluid.

In carrying out the desulfurizing of a hydrocarbon-containing fluid, it is presently preferred that an agent be employed which interferes with any possible chemical or physical reacting of the olefinic and aromatic compounds in the hydrocarbon-containing fluid which is being treated with a sorbent composition of the present invention. Preferably, such agent is hydrogen.

Hydrogen flow in the desulfurization zone is generally such that the mole ratio of hydrogen to hydrocarbon-containing fluid is the range of from about 0.1 to about 10, preferably in the range of from about 0.2 to about 3.

The desulfurization zone can be any zone wherein desulfurizing a hydrocarbon-containing fluid such as cracked-gasoline, diesel fuel or the like can take place. The regeneration zone can be any zone wherein regenerating or desulfurizing a sulfurized sorbent composition can take place. The activation zone can be any zone wherein activating, i.e., reducing, a regenerated, desulfurized sorbent composition can take place. Examples of suitable zones are fixed bed reactors, moving bed reactors, fluidized bed reactors, transport reactors, reactor vessels and the like.

If desired, during the desulfurizing of a hydrocarbon-containing fluid according to a process of the present invention, a diluent such as methane, carbon dioxide, flue gas, nitrogen and the like and combinations thereof can be used. Thus, it is not essential to the practice of a process of the present invention that a high purity hydrogen be employed in achieving the desired desulfurization of a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel.

It is presently preferred, when utilizing a fluidized bed reactor system, that a

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sorbent composition be used having a mean particle size, as described herein, in the range of from about 1 micrometer to about 1000 micrometers. Preferably, such sorbent composition has a mean particle size in the range of from about 5 micrometers to about 500 micrometers and, more preferably, in the range of from 10 micrometers to 200
5 micrometers. When a fixed bed reactor system is employed for the practice of a process of the present invention, the sorbent composition should generally have a particulate size in the range of from about 1/32 inch to about 1/2 inch diameter, preferably in the range of from about 1/32 inch to about 1/4 inch diameter.

It is further presently preferred to use a sorbent composition having a surface area
10 in the range of from about 1 square meter per gram to about 1000 square meters per gram (m^2/g), preferably in the range of from about 1 m^2/g to about 800 m^2/g .

The separating of the desulfurized hydrocarbon-containing fluid, preferably gaseous or vaporized desulfurized hydrocarbon-containing fluid, and sulfurized sorbent composition can be accomplished by any manner or method known in the art that can
15 separate a solid from a gas. Examples of suitable separating means for separating solids and gases include, but are not limited to, cyclonic devices, settling chambers, impingement devices, filters, and the like and combinations thereof. The desulfurized hydrocarbon-containing fluid, preferably desulfurized gaseous cracked-gasoline or desulfurized gaseous diesel fuel, can then be recovered and preferably liquefied.
20 Liquefaction of such desulfurized hydrocarbon-containing fluid can be accomplished by any manner or method known in the art.

The hydrocarbon-containing fluid as described herein, preferably gaseous cracked-gasoline or gaseous diesel fuel, suitable as a feed in a process of the present invention is a composition that comprises olefins, aromatics, sulfur, as well as paraffins
25 and naphthenes.

The amount of olefins in gaseous cracked-gasoline is generally in the range of from about 10 to about 35 weight percent olefins based on the total weight of the gaseous cracked-gasoline. For diesel fuel there is essentially no olefin content.

The amount of aromatics in gaseous cracked-gasoline is generally in the range of
30 from about 20 to about 40 weight percent aromatics based on the total weight of the gaseous cracked-gasoline. The amount of aromatics in gaseous diesel fuel is generally in

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the range of from about 10 to about 90 weight percent aromatics based on the total weight of the gaseous diesel fuel.

5 The amount of sulfur in the hydrocarbon-containing fluid, preferably cracked-gasoline or diesel fuel, suitable for use in a process of the present invention can be in the range of from about 100 parts per million sulfur by weight of the cracked-gasoline to about 10,000 parts per million sulfur by weight of the cracked-gasoline and from about 100 parts per million sulfur by weight of the diesel fuel to about 50,000 parts per million sulfur by weight of the diesel fuel prior to the treatment of such hydrocarbon-containing fluid with a process of the present invention.

10 The amount of sulfur in the desulfurized hydrocarbon-containing fluid, such as desulfurized cracked-gasoline or desulfurized diesel fuel, following treatment in accordance with a process of the present invention is less than about 100 parts per million (ppm) sulfur by weight of hydrocarbon-containing fluid, preferably less than about 90 ppm sulfur by weight of hydrocarbon-containing fluid, and more preferably less than
15 about 80 ppm sulfur by weight of hydrocarbon-containing fluid.

In carrying out a process of the present invention, if desired, a stripper zone can be inserted before and/or after the regenerating of the sulfurized sorbent composition. Such stripper zone, preferably utilizing a stripping agent, will serve to remove a portion, preferably all, of any hydrocarbon(s) from the sulfurized sorbent composition. Such
20 stripper zone can also serve to remove oxygen and sulfur dioxide from the system prior to introduction of the regenerated sorbent composition into the activation zone. Such stripping employs a set of conditions that includes total pressure, temperature, and stripping agent partial pressure.

Preferably, the stripping, when employed, is carried out at a total pressure in the
25 range of from about 25 pounds per square inch absolute (psia) to about 500 psia. The temperature for such stripping can be in the range of from about 100°F to about 1000°F. Such stripping is carried out for a time sufficient to achieve the desired level of stripping. Such stripping can generally be achieved in a time period in the range of from about 0.1 hour to about 4 hours, preferably in the range of from about 0.3 hour to about 1 hour.

30 The stripping agent is a composition(s) that helps to remove a hydrocarbon(s) from the sulfurized sorbent composition. Preferably, the stripping agent is nitrogen.

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The regenerating is carried out under a set of conditions that includes total pressure and sulfur removing agent partial pressure. Total pressure is generally in the range of from about 25 pounds per square inch absolute (psia) to about 500 psia.

The sulfur removing agent partial pressure is generally in the range of from about
5 1 percent to about 100 percent of the total pressure.

The sulfur removing agent, i.e., regenerating agent, is a composition(s) that helps to generate gaseous sulfur-containing compounds and oxygen-containing compounds such as sulfur dioxide, as well as to burn off any remaining hydrocarbon deposits that might be present. The preferred sulfur removing agent, i.e., regenerating agent, suitable
10 for use in the regeneration zone is oxygen or an oxygen-containing gas(es) such as air. Such regeneration is carried out for a time sufficient to achieve the desired level of regeneration. Such regeneration can generally be achieved in a time period in the range of from about 0.1 hour to about 24 hours, preferably in the range of from about 0.5 hour to about 3 hours.

15 The regenerating is carried out at a temperature generally in the range of from about 100°F to about 1500°F, preferably in the range of from about 800°F to about 1200°F.

The desulfurized sorbent composition is then subjected to activating, i.e., reducing, in an activation zone with a reducing agent, preferably hydrogen, so that at least
20 a portion of the promoter component, preferably comprising nickel, incorporated on, in, or with the sorbent composition is reduced to thereby provide a sorbent composition comprising a reduced-valence promoter component, preferably reduced nickel. Such sorbent composition comprises a reduced-valence promoter component, preferably reduced nickel, incorporated on, in, or with such sorbent composition in an amount that
25 provides for the removal of sulfur from a hydrocarbon-containing fluid such as cracked-gasoline or diesel fuel according to a process of the present invention.

In general, when practicing a process of the present invention, the activating, i.e., reducing, of the regenerated, desulfurized sorbent composition is carried out at a temperature in the range of from about 100°F to about 1500°F and at a pressure in the
30 range of from about 15 pounds per square inch absolute (psia) to about 1500 psia. Such reduction is carried out for a time sufficient to achieve the desired level of promoter

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component reduction. Such reduction can generally be achieved in a time period in the range of from about 0.01 hour to about 20 hours.

Following the activating, i.e., reducing, of the regenerated, desulfurized sorbent composition, at least a portion of the resulting activated (i.e., reduced) sorbent
5 composition can be returned to the desulfurization zone.

When carrying out a process of the present invention, the steps of desulfurizing, regenerating, activating (i.e., reducing), and optionally stripping before and/or after such regenerating, can be accomplished in a single zone or vessel or in multiple zones or vessels.

10 When carrying out a process of the present invention in a fixed bed reactor system, the steps of desulfurizing, regenerating, activating, and optionally stripping before and/or after such regenerating are accomplished in a single zone or vessel.

When carrying out a process of the present invention in a fluidized bed reactor system, the steps of desulfurizing, regenerating, activating, and optionally stripping before
15 and/or after such regenerating are accomplished in multiple zones or vessels.

When a desulfurized hydrocarbon-containing fluid resulting from the practice of a process of the present invention is a desulfurized cracked-gasoline, such desulfurized cracked-gasoline can be used in the formulation of gasoline blends to provide gasoline products suitable for commercial consumption and can also be used where a cracked-
20 gasoline containing low levels of sulfur is desired.

When a desulfurized hydrocarbon-containing fluid resulting from the practice of a process of the present invention is a desulfurized diesel fuel, such desulfurized diesel fuel can be used in the formulation of diesel fuel blends to provide diesel fuel products suitable for commercial consumption and can also be used where a diesel fuel containing
25 low levels of sulfur is desired.

The following examples are presented to further illustrate this invention and are not to be construed as unduly limiting the scope of this invention.

EXAMPLE I

30 Sorbent A (Control) was a spray-dried sorbent material prepared in the following manner. A 20 gram quantity of sodium pyrophosphate was dissolved in 2224 grams of

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distilled water to provide a solution. To the solution was added 200 grams of Vista DISPAL 180 alumina with vigorous stirring. While the alumina slurry was being mixed with a high shear mixer, a 628 gram quantity of Celite Filter Cel (Celite Corporation, Lompoc, California) and a 788 gram quantity of zinc oxide were added to the slurry and
5 further mixed for about 15 minutes. The resulting mixed slurry was sieved through a 25 mesh screen. The resulting sieved slurry was then spray-dried using a Niro Mobile Minor spray dryer equipped with a fountain head (Niro, Inc., Columbia, Maryland). The operating conditions of the spray dryer included an inlet temperature of 320°C and an outlet temperature of about 100°C to about 120°C. The spray-dried material was then
10 dried in an oven at 150°C for three hours and then calcined at 635°C for one hour to thereby obtain a dried and calcined spray-dried sorbent material.

A 100 gram quantity of the thus dried and calcined spray-dried sorbent material (149 micron to 74 micron fraction) was then spray impregnated with a solution of 59.4 grams of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 62.9 grams of distilled water.
15 The thus-impregnated material was then dried in an oven which was increased from an ambient temperature at 3°C per minute to 150°C and maintained at 150°C for three hours and then increased at a rate of 3°C per minute to 635°C and maintained at 635°C for one hour to thereby obtain a nickel-impregnated spray-dried sorbent material.

A 50 gram quantity of the thus dried and calcined nickel-impregnated spray-dried
20 sorbent material was then spray impregnated with a solution of 37.1 grams of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 7.5 grams of distilled water. The thus-impregnated material was then dried in an oven which was increased from an ambient temperature at 3°C per minute to 150°C and maintained at 150°C for three hours and then increased at a rate of 3°C per minute to 635°C and maintained at 635°C for one
25 hour to thereby obtain a twice-nickel-impregnated spray-dried sorbent material (Control Sorbent A). Control Sorbent A contained a final total of about 21 weight percent nickel based on the total weight of the material. The physical and chemical characteristics of Control Sorbent A are included in Table I. The Davison Index, as described herein, was determined using a 5 gram quantity of -100 to +200 mesh fraction of Control Sorbent A.

30 Sorbent B (Invention) was a spray-dried sorbent material prepared in the following manner. A 20 gram quantity of sodium pyrophosphate was dissolved in 3000 grams of

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distilled water to provide a solution. To the solution was added 200 grams of Vista DISPAL 180 alumina with vigorous stirring. While the alumina slurry was being mixed using a high shear mixer, a 314 gram quantity of Celite Filter Cel (Celite Corporation, Lompoc, California) and a 788 gram quantity of zinc oxide were added to the slurry and
5 further mixed for about 20 minutes. A 187.2 gram quantity of bentonite 325 and an additional 1000 gram quantity of distilled water were then added to the slurry. The resulting mixed slurry was sieved through a 25 mesh screen. The resulting sieved material was then spray-dried using a Niro Mobile Minor spray dryer equipped with a fountain head (Niro, Inc., Columbia, Maryland). The operating conditions of the spray
10 dryer included an inlet temperature of 320°C and an outlet temperature of about 100°C to about 120°C. The spray-dried material was then dried in an oven at 150°C and then calcined at 635°C for one hour to thereby obtain a dried and calcined spray-dried sorbent material.

A 100 gram quantity of the thus dried and calcined spray-dried sorbent material
15 (149 micron to 74 micron fraction) was then spray impregnated with a solution of 59.4 grams of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 20.4 grams of distilled water. The thus-impregnated material was then dried in an oven which was increased from an ambient temperature at 3°C per minute to 150°C and maintained at 150°C for one hour and then increased at a rate of 3°C per minute to 635°C and maintained at 635°C for one
20 hour to thereby obtain a nickel-impregnated spray-dried sorbent material.

A 50 gram quantity of the thus dried and calcined nickel-impregnated spray-dried sorbent material was then spray impregnated with a solution of 22.3 grams of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 13 grams of distilled water. The resulting twice-nickel-impregnated spray-dried material was then dried in an oven which was increased
25 from an ambient temperature at 3°C per minute to 150°C and maintained at 150°C for one hour and then increased at a rate of 3°C per minute to 635°C and maintained at 635°C for one hour to thereby obtain a twice-nickel-impregnated spray-dried sorbent material.

A 54.4 gram quantity of such twice-nickel-impregnated spray-dried sorbent material was then spray impregnated with a solution of 24.2 grams of nickel nitrate
30 hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 12.2 grams of distilled water. The resulting material was then dried in an oven which was increased from an ambient temperature at 3°C per

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minute to 150°C and maintained at 150°C for one hour and then increased at a rate of 3°C per minute to 635°C and maintained at 635°C for one hour to thereby obtain a thrice-nickel-impregnated spray-dried sorbent material (Invention Sorbent B). Invention Sorbent B contained a final total of about 23 weight percent nickel based on the total weight of the material and about 10 weight percent bentonite based on the total weight of the material.

The physical and chemical characteristics of Invention Sorbent B are included in Table I. The Davison Index, as described herein, was determined using a 5 gram quantity of -100 to +200 mesh fraction of Invention Sorbent B.

10

TABLE I

Particle Size Distribution (%)	Control Sorbent A (No Attrition-Resistance-Enhancing Component)	Invention Sorbent B (With Attrition-Resistance-Enhancing Component)
>297 microns	1.0	14.5
149 microns	57.8	25.8
105 microns	39.9	19.7
88 microns	1.2	13.0
74 microns	0.1	22.0
53 microns	0	3.1
<53 microns	0	2.9
Davison Index	19	9

15

20

EXAMPLE II

This example illustrates the performance of Control Sorbent A and Invention Sorbent B described herein in Example I in a desulfurization process.

Ten grams of Control Sorbent A were placed on a frit in a 1-inch diameter quartz reactor tube having a length of about 12 inches.

During each cycle, gaseous cracked-gasoline was pumped upwardly through the reactor at a rate of 13.4 milliliters per hour (mL/HR). The gaseous cracked-gasoline had a motor octane number (MON) of 80, an olefin content of 24.9 weight percent, 340 parts per million sulfur by weight sulfur-containing compounds based on the total weight of the gaseous cracked-gasoline, and about 95 weight percent thiophenic compounds (such as,

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for example, alkyl benzothiophenes, alkyl thiophenes, benzothiophenes and thiophenes) based on the weight of sulfur-containing compounds in the gaseous cracked-gasoline.

During each cycle, the reactor was maintained at a temperature of 700°F and at a pressure of 15 pounds per square inch absolute (psia). Hydrogen flow was at 150 standard cubic centimeters per minute (sccm) diluted with 150 sccm of nitrogen.

Before Cycle 1 was initiated, Control Sorbent A was reduced with hydrogen flowing at a rate of 300 sccm at a temperature of 700°F for a period of one hour. Each cycle consisted of four hours with the product sulfur (ppm) for each cycle being measured at one hour intervals over each four-hour cycle period. After each cycle, Control Sorbent A was regenerated at 900°F for 1.5 hours with a mixture of oxygen and nitrogen containing four volume percent oxygen, then purged with nitrogen, and then reduced in hydrogen flowing at a rate of 300 sccm for one hour at 700°F. Control Sorbent A was tested over two cycles.

The above-described testing procedure was then repeated in the same manner with the exception that Invention Sorbent B was used in place of Control Sorbent A and was tested over eight cycles.

The results of the test for Control Sorbent A are shown below in Table II. The results of the test for Invention Sorbent B are shown below in Table III.

TABLE II		
Control Sorbent A (No Attrition-Resistance-Enhancing Component)		
	Cycle 1	Cycle 2
TOS ¹	SULFUR (ppm) IN THE PRODUCT	
1 hr	10	5
2 hr	20	20
3 hr	25	15
4 hr	20	15

¹ TOS denotes Time on Stream in hours

TABLE III Invention Sorbent B (With Attrition-Resistance-Enhancing Component)								
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8
5 TOS ¹	*****SULFUR (ppm) IN THE PRODUCT *****							
1 hr	15	10	<5	10	5	40	10	<5
2 hr	15	15	15	25	20	45	30	5
3 hr	10	10	15	25	15	35	40	10
10 4 hr	-- ²	10	10	15	10	20	30	5

¹ TOS denotes Time on Stream in hours

² Not Determined

The test data clearly demonstrate that use of a sorbent composition of the present invention to remove sulfur from cracked-gasoline containing 340 parts per million sulfur by weight sulfur-containing compounds based on the total weight of the cracked-gasoline results in a significant reduction of the sulfur content of such cracked-gasoline, generally to a level of about 5 to 45 parts per million sulfur.

The test data further demonstrate that a sorbent composition which contained about 10 weight percent of an attrition-resistance-enhancing component (bentonite) distributed throughout a sorbent composition prepared according to a process of the present invention desulfurized the cracked-gasoline as effectively as Control Sorbent A, while Invention Sorbent B exhibited superior attrition resistance.

The data also clearly show that Invention Sorbent B which contained an attrition-resistance-enhancing component (bentonite), exhibited a very high effectiveness to remove sulfur which was comparable to Control Sorbent A which did not contain an attrition-resistance-enhancing component, yet Invention Sorbent B exhibited superior attrition resistance properties. Invention Sorbent B exhibited excellent sulfur removal performance and little or no loss in sulfur removal efficiency during the 8 cycles of operation conducted in Example II. The improvement in sorbent attrition resistance is believed to be due to a novel process of making the inventive sorbent composition by a process of utilizing an attrition-resistance-enhancing component and a support component to provide a material which is subsequently promoted with a promoter component and then reduced to produce a sorbent composition with enhanced attrition resistance

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compared to a sorbent composition which does not contain such attrition-resistance-enhancing component.

5 The difference in performance between Invention Sorbent B and Control Sorbent A is certainly unexpected. One would not expect that contacting a support component and an attrition-resistance-enhancing component followed by promoting with a promoter component and then reducing to produce a sorbent composition would enhance the performance of such sorbent composition in terms of attrition resistance, yet, at a desulfurization effectiveness comparable to a sorbent which does not contain such attrition-resistance-enhancing component. The results demonstrate that the inventive
10 sorbent composition, containing an attrition-resistance-enhancing component, is significantly superior to a sorbent which does not contain such attrition-resistance-enhancing component.

 The data also clearly show that Invention Sorbent B was highly effective in sulfur removal. Even after 8 cycles of operation, the amount of sulfur removed was very high.

15 The results shown in the above examples clearly demonstrate that the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those inherent therein.

 Reasonable variations, modifications, and adaptations can be made within the scope of this disclosure and the appended claims without departing from the scope of this
20 invention.

CLAIMS

1. A process of making a sorbent composition comprising:
contacting a support component and an attrition-resistance-enhancing component
to form a mixture;
5 particulating said mixture to thereby provide a particulate;
incorporating said particulate with a promoter component to thereby provide a
promoted particulate; and
reducing said promoted particulate.
2. A process according to claim 1, wherein said attrition-resistance-enhancing
10 component is selected from the group consisting of clays, high alumina cements, natural
cements, portland cement, calcium aluminate, calcium silicate, talc, and combinations
thereof.
3. A process according to claim 1, wherein said attrition-resistance-enhancing
component is selected from the group consisting of bentonite, sodium bentonite,
15 acid-washed bentonite, atapulgite, china clay, kaolinite, montmorillonite, illite, halloysite,
hectonite, sepiolite, and combinations thereof.
4. A process according to claim 1, wherein said attrition-resistance-enhancing
component is selected from the group consisting of bentonite, sodium bentonite,
acid-washed bentonite, and combinations thereof.
- 20 5. A process according to claim 1, wherein said attrition-resistance-enhancing
component is bentonite.
6. A process according to claim 1, wherein said promoter component is selected
from the group consisting of metals, metal oxides, and combinations thereof.
7. A process according to claim 6, wherein said metals are selected from the group
25 consisting of cobalt, nickel, iron, manganese, copper, zinc, molybdenum, tungsten, silver,
tin, vanadium, antimony, and combinations thereof.
8. A process according to claim 7, wherein said metal oxides are selected from the
group consisting of cobalt oxides, nickel oxides, iron oxides, manganese oxides, copper
oxides, zinc oxides, molybdenum oxides, tungsten oxides, silver oxides, tin oxides,
30 vanadium oxides, antimony oxides, and combinations thereof.
9. A process according to claim 6, wherein said metals are in a form selected from

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the group consisting of metal acetates, metal carbonates, metal nitrates, metal sulfates, metal thiocyanates, and combinations thereof.

10. A process according to claim 1, wherein said promoter component is selected from the group consisting of nickel, cobalt, and combinations thereof.
- 5 11. A process according to claim 1, wherein said promoter component is nickel.
12. A process according to claim 1, wherein said promoter component comprises a precursor of a nickel oxide.
13. A process according to claim 1, wherein said promoter component comprises nickel nitrate hexahydrate.
- 10 14. A process according to claim 1, wherein said support component comprises zinc oxide, inorganic carriers, organic carriers, and combinations thereof.
15. A process according to claim 1, wherein said support component comprises zinc oxide, silica, and alumina.
16. A process according to claim 15, wherein said zinc oxide comprises powdered
15 zinc oxide or one or more zinc compounds that are convertible to zinc oxide.
17. A process according to claim 15, wherein said silica is selected from the group consisting of diatomite, expanded perlite, silicalite, silica colloid, flame-hydrolyzed silica, hydrolyzed silica, silica gel, precipitated silica, silicon compounds, and combinations thereof and further wherein said silicon compounds are selected from the group consisting
20 of silicic acid, ammonium silicate, and combinations thereof.
18. A process according to claim 15, wherein said silica is diatomite or expanded perlite.
19. A process according to claim 15, wherein said alumina is present in said silica or is selected from the group consisting of colloidal alumina solutions, hydrated aluminas,
25 and alumina compounds produced by the dehydration of alumina hydrates, or both.
20. A process according to claim 1, wherein said support component comprises zinc oxide, silica, and alumina and further wherein said zinc oxide is present in said sorbent composition in an amount in the range of from about 10 to about 90 weight percent zinc oxide based on the total weight of the sorbent composition, said silica is present in said
30 sorbent composition in an amount in the range of from about 5 to about 85 weight percent silica based on the total weight of the sorbent composition, and said alumina is present in

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said sorbent composition in an amount in the range of from about 0.1 to about 30 weight percent alumina based on the total weight of said sorbent composition.

21. A process according to claim 20, wherein said attrition-resistance-enhancing component is present in said sorbent composition in an amount in the range of from about 1 to about 30 weight percent attrition-resistance-enhancing component based on the total weight of said sorbent composition.

22. A process according to claim 21, wherein said promoter component is present in said sorbent composition in an amount in the range of from about 5 to about 50 weight percent promoter component based on the total weight of said sorbent composition.

23. A process according to claim 1, wherein said promoter component comprises a bimetallic promoter component and further wherein said bimetallic promoter component comprises nickel and cobalt in a weight ratio in the range of from about 20:1 to about 1:20.

24. A process according to claim 1, wherein said sorbent composition comprises zinc oxide in an amount in the range of from about 35 to about 50 weight percent zinc oxide based on the total weight of the sorbent composition, silica in an amount in the range of from about 30 to about 40 weight percent silica based on the total weight of the sorbent composition, alumina in an amount in the range of from about 6 to about 12 weight percent alumina based on the total weight of the sorbent composition, bentonite in an amount in the range of from about 2 to about 12 weight percent bentonite based on the total weight of the sorbent composition, and nickel, prior to reduction to zero valence, in an amount in the range of from about 14 to about 30 weight percent nickel based on the total weight of the sorbent composition.

25. A process according to claim 1, wherein said mixture is selected from the group consisting of a wet mix, a dough, a paste, and a slurry, and said particulate is selected from the group consisting of a granulate, an extrudate, a tablet, a sphere, a pellet, and a micro-sphere.

26. A process according to claim 1, wherein said particulate comprises a micro-sphere.

27. A process according to claim 1, wherein said mixture is in the form of a slurry and said particulating comprises spray drying said slurry to form a micro-sphere.

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28. A process according to claim 27, wherein said micro-sphere has a mean particle size in the range of from about 1 micrometer to about 1000 micrometers.

29. A process according to claim 1, wherein said particulate is subjected to drying under a drying condition and calcining under a calcining condition before said

5 incorporating.

30. A process according to claim 29, wherein said drying condition comprises a temperature in the range of from about 82.2°C to about 143.3°C (about 180°F to about 290°F), a time period in the range of from about 0.5 hour to about 60 hours, and a pressure in the range of from about atmospheric to 1,033 kPa (about 150 pounds per square inch absolute), and further wherein said calcining condition comprises a
10 temperature in the range of from about 204°C to about 982.2°C (about 400°F to about 1800°F), a time period in the range of from about 1 hour to about 60 hours, and a pressure in the range of from about 48.2 kPa to about 5,167 kPa (about 7 pounds per square inch absolute to about 750 pounds per square inch absolute).

15 31. A process according to claim 1, wherein said promoted particulate is subjected to drying under a drying condition and calcining under a calcining condition before said reducing.

32. A process according to claim 31, wherein said drying condition comprises a temperature in the range of from about 82.2°C to about 143.3°C (about 180°F to about
20 290°F), a time period in the range of from about 0.5 hour to about 60 hours, and a pressure in the range of from about atmospheric to about 1,033 kPa (about 150 pounds per square inch absolute), and further wherein said calcining condition comprises a temperature in the range of from about 204°C to about 982.2°C (about 400°F to about 1800°F), a time period in the range of from about 1 hour to about 60 hours, and a pressure
25 in the range of from about 48.2 kPa to about 5,167 kPa (about 7 pounds per square inch absolute to about 750 pounds per square inch absolute).

33. A process according to claim 1, wherein said sorbent composition has a Davison Index value in the range of from about 1 to about 25.

34. A process according to claim 1, wherein said incorporating is selected from the
30 group consisting of impregnating, soaking, spraying, and combinations thereof.

35. A process according to claim 1, wherein said incorporating comprises incipient

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wetness impregnation.

36. A composition prepared by the process of any one of the preceding claims.

37. A process for the removal of sulfur from a hydrocarbon-containing fluid comprising cracked-gasoline or diesel fuel wherein said process comprises:

5 desulfurizing, in a desulfurization zone, said hydrocarbon-containing fluid with a sorbent composition to thereby provide a desulfurized hydrocarbon-containing fluid and a resulting sulfurized sorbent composition;

separating said desulfurized hydrocarbon-containing fluid and said resulting sulfurized sorbent composition;

10 regenerating, in a regeneration zone, at least a portion of said resulting sulfurized sorbent composition to thereby provide a regenerated, desulfurized, sorbent composition;

reducing, in an activation zone, at least a portion of said regenerated, desulfurized, sorbent composition to thereby provide a reduced, regenerated, desulfurized sorbent composition; and

15 returning at least a portion of said reduced, regenerated, desulfurized sorbent composition to said desulfurization zone;

and further wherein said sorbent composition is prepared by the process of any one of preceding claims 1-35.

38. A process according to claim 37, wherein said desulfurizing is carried out at a
20 temperature in the range of from about 37.7°C to about 537.7°C (about 100°F to about 1000°F) and at a pressure in the range of from about 103.3 kPa to about 10,335 kPa (about 15 pounds per square inch absolute to about 1500 pounds per square inch absolute) for a time sufficient to effect the removal of sulfur from said hydrocarbon-containing fluid.

25 39. A process according to claim 38, wherein said regenerating is carried out at a temperature in the range of from about 37.7°C to about 815.5°C (about 100°F to about 1500°F) and at a pressure in the range of from about 172.2 kPa to about 3,445 kPa (about 25 pounds per square inch absolute to about 500 pounds per square inch absolute) for a time sufficient to effect the removal of at least a portion of sulfur from said resulting
30 sulfurized sorbent composition.

40. A process according to claim 39, wherein air is employed as a regeneration agent

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in said regeneration zone.

41. A process according to claim 39, wherein said reducing comprises using hydrogen and further wherein said reducing is carried out at a temperature in the range of from about 37.7°C to about 815.5°C (about 100°F to about 1500°F) and at a pressure in the
5 range of from about 103.3 kPa to about 10,335 kPa (about 15 pounds per square inch absolute to about 1500 pounds per square inch absolute) and for a time sufficient to effect a reduction of the valence of said promoter component of said sorbent composition.

42. A process according to claim 41, wherein said resulting sulfurized sorbent composition is subjected to stripping prior to introduction to said regeneration zone.

10 43. A process according to claim 41, wherein said regenerated, desulfurized, sorbent composition is subjected to stripping prior to introduction to said activation zone.

44. A process according to claim 37, wherein said hydrocarbon-containing fluid is cracked-gasoline.

45. The cracked-gasoline product of the process for the removal of sulfur of claim 37.

15 46. A sorbent composition suitable for removal of sulfur from a hydrocarbon-containing fluid comprising cracked-gasoline or diesel fuel wherein said sorbent composition comprises a support component, an attrition-resistance-enhancing component, and a promoter component wherein said promoter component is present in a substantially reduced valence state and in an amount which will effect the removal of said
20 sulfur from said hydrocarbon-containing fluid when said hydrocarbon-containing fluid is contacted with said sorbent composition under desulfurization conditions.

47. A sorbent composition according to claim 46, wherein said support component comprises zinc oxide, silica, and alumina, and further wherein said attrition-resistance-enhancing component is selected from the group consisting of bentonite, sodium
25 bentonite, acid-washed bentonite, atapulgite, china clay, kaolinite, montmorillonite, illite, halloysite, hectonite, sepiolite, and combinations thereof, and further wherein said promoter component is selected from the group consisting of metals, metal oxides, and combinations thereof.

48. A sorbent composition according to claim 47, wherein said metals are selected
30 from the group consisting of cobalt, nickel, iron, manganese, copper, zinc, molybdenum, tungsten, silver, tin, vanadium, antimony, and combinations thereof and said metal oxides

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are selected from the group consisting of cobalt oxides, nickel oxides, iron oxides, manganese oxides, copper oxides, zinc oxides, molybdenum oxides, tungsten oxides, silver oxides, tin oxides, vanadium oxides, antimony oxides, and combinations thereof.

35 49. A sorbent composition according to claim 48, wherein said attrition-resistance-enhancing component is bentonite and further wherein said promoter component is nickel.

40 50. A sorbent composition according to claim 46, wherein said attrition-resistance-enhancing component is present in said sorbent composition in an amount in the range of from about 1 to about 30 weight percent attrition-resistance-enhancing component based on the total weight of said sorbent composition and further wherein said promoter component is present in said sorbent composition in an amount in the range of from about 5 to about 50 weight percent promoter component based on the total weight of said sorbent composition.

45 51. A sorbent composition according to claim 46, wherein said promoter component comprises a bimetallic promoter component and further wherein said bimetallic promoter component comprises nickel and cobalt in a weight ratio in the range of from about 20:1 to about 1:20.

50 52. A sorbent composition according to claim 46, wherein said sorbent composition comprises zinc oxide in an amount in the range of from about 35 to about 50 weight percent zinc oxide based on the total weight of the sorbent composition, silica in an amount in the range of from about 30 to about 40 weight percent silica based on the total weight of the sorbent composition, alumina in an amount in the range of from about 6 to about 12 weight percent alumina based on the total weight of the sorbent composition, 55 bentonite in an amount in the range of from about 2 to about 12 weight percent bentonite based on the total weight of the sorbent composition, and nickel, prior to reduction to zero valence, in an amount in the range of from about 14 to about 30 weight percent nickel based on the total weight of the sorbent composition.

60 53. A sorbent composition according to claim 46, wherein said sorbent composition has a Davison Index value in the range of from about 1 to about 25.

54. A sorbent composition according to claim 46, wherein said sorbent composition comprises a micro-sphere having a mean particle size in the range of from about 1 micro-

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meter to about 1000 micrometers.

65 55. A sorbent composition according to claim 46, wherein said sorbent composition has been reduced with a reducing agent to thereby provide a sorbent composition having a reduced-valence promoter component and further wherein said reduced-valence promoter component is present in an amount in the range of from about 5 to about 50 weight percent of the total weight of said sorbent composition.

70 56. A sorbent composition according to claim 55, wherein said reducing agent is hydrogen.

57. A sorbent composition according to claim 55, wherein said reduced-valence promoter component is reduced nickel.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/26062

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 25/02, 25/12, 29/00, 29/04, 29/16; B01J 20/06, 20/08, 20/10, 20/12, 20/30, 20/34
US CL : 208/208R, 244, 245, 246, 247, 248, 249, 299, 307; 502/405, 406, 407, 415

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/208R, 244, 245, 246, 247, 248, 249, 299, 307; 502/405, 406, 407, 415

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST search terms: adsorbent, sorbent, nickel, clay, zinc oxide, silica, alumina desulfurization

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,914,292 A (KHARE et al) 22 June 1999 (22.06.1999), see column 4, line 65 through column 6, line 50; column 8, line 40 through column 9, line 33; column 11, lines 6-22; and column 12, lines 52-65.	1-44, 46-57
Y	US 4,419,224 A (MILLER et al) 06 December 1983 (06.12.1983), see column 3, line 27 through column 4, line 13.	1-44, 46-57
X	US 2,951,034 A (STUART) 30 August 1960 (30.08.1960). See column 1, lines 46-56; column 2, lines 16-33; column 3, lines 4-17; and column 4, lines 3-6.	45
Y		1-44, 46-57
A	US 6,056,871 A (KHARE et al) 02 May 2000 (02.05.2000).	1-57

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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document member of the same patent family

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